

Check of Silver, Platinum and Gold Electrodes

Of interest to:
General analytical; H 1

Summary

Methods for testing the condition of metal electrodes are presented.

Pt and Au electrodes can be tested with the Metrohm ready-to-use redox standard 6.2306.020. Alternatively, the potential of quinhydrone saturated in buffer can be measured and compared to theoretical values.

All electrodes can be checked by titration. For Ag electrodes a determination of hydrochloric acid with silver nitrate is performed, for Pt and Au electrodes a iodine solution is titrated with sodium thiosulfate. An appropriate criterion is the titration duration, which should not exceed 150s for the Ag- and Pt-DET titration and 160s for the Au-MET titration.

Instruments and accessories

- Titrino/ Titrande with stirrer and dosing unit
- Or pH Meter with stirrer for measurement with the redox standards
- Metal electrodes to be tested:
 - 6.043x.xx0 Ag, Pt or Au Titrode
 - 6.045x.100 Combined Ag-, Pt- or Au-ring electrode
 - 6.035x.100 Separate Ag-, Pt- or Au-ring electrode
 - 6.1248.xxx Electrode rod Ag, Pt or Au
- 6.07xx.xxx Reference electrode
- 6.1418.2x0 Titration vessel with thermostat jacket
- 6.1414.010 Titration vessel lid
- Water bath for the check with redox standards

Reagents

Electrolyte:

- 6.2310.000 KNO_3 sat. for Ag electrodes
- 6.2308.020 $c(\text{KCl}) = 3 \text{ mol/L}$ for Pt and Au electrodes

Check with redox standard

- 6.2306.20 Redox standard $U = + 250 \pm 5 \text{ mV}$

Or prepared with

- Ultra pure quinhydrone
- 6.2307.110 Buffer solution $\text{pH} = 7.00$
- and/or 6.2307.100 Buffer solution $\text{pH} = 4.00$

Check by titration

Electrode	Ag	Pt/ Au
Sample	HCl	I_2
Concentration [mol/ L]	0.1	0.05
Titration	AgNO_3	Na_2SO_3
Concentration [mol/ L]	0.1	0.1
Auxiliary solution	-	H_2SO_4
Concentration [mol/ L]	-	0.1

Analysis

1) Check with redox standard solution

Electrodes:

- 6.045x.xxx Combined Pt- or Au-ring electrode
- 6.035x.xxx Separate Pt- or Au-ring electrode
- 6.1248.xxx Electrode rod Pt or Au

Only Pt- and Au-electrodes can be tested with the standard solution due to oxidation of less noble metals like silver.

a) Check with ready-to-use redox standard solution 6.2306.20

The electrode is checked with the ready-to-use, certified redox standard solution Metrohm 6.2306.020. Against the reference system $\text{Ag}/\text{AgCl}/c(\text{KCl}) = 3 \text{ mol/L}$, this standard has a redox potential of $U = + 250 \text{ mV} \pm 5 \text{ mV}$ at 20°C .

The redox standard is first temperate at 20°C using a water bath. When 20°C have been reached, the potential of the solution is measured with the electrode to be tested while stirring. The deviation from the certified value should not exceed 5 mV. For example the measured value of a certified standard of 253.5 mV should range between 248.5 and 258.5 mV.

b) Check with self-made redox standard solution

A saturated solution of quinhydrone in acidic or neutral (but not alkaline) buffer solution represents a well-defined redox system.

The buffer solution is mixed with little ultrapure quinhydrone and shaken briefly until saturation is obtained; some excess undissolved quinhydrone must remain. The electrode assembly to be checked is immersed in the solution. The potential is measured and compared with the calculated theoretical values from Table 1.

Table 1: Potential of an electrode in a buffer solution saturated with quinhydrone

Metrohm buffer, saturated with quinhydrone	T [°C]	U [mV]
pH = 4.0	5	+ 273.2
	15	+ 264.9
	20	+ 260.8
	25	+ 266.1
	30	+ 252.0
pH = 7.0	5	+ 102.7
	15	+ 90.5
	20	+ 84.6
	25	+ 78.6
	30	+ 72.2

The potential of the reference system Ag/AgCl has been taken into account. The electrode is filled with $c(\text{KCl}) = 3 \text{ mol/L}$.

Remarks

If deviations from the theoretical value exceed $\pm 5 \text{ mV}$, the potential of the reference electrode used must be measured against a second reference electrode known to be reliable. The reference electrode being tested is in good shape if the measured potential is zero.

A precious metal electrode that measures an incorrect potential is defective or contaminated in some way. Directions for cleaning of such electrodes are given in the corresponding instructions for use and monographs.

2) Check with titration

Electrodes:

6.043x.xxx	Ag, Pt or Au Titrode
6.045x.xxx	Combined Ag-, Pt- or Au-ring electrode
6.035x.xxx	Separate Ag-, Pt- or Au-ring electrode
6.1248.xxx	Electrode rod Ag, Pt or Au

A 100 mL beaker is filled with 50 mL deionised water. For checking a Pt or Au electrode, 1 mL of sulphuric acid is added supplementary. Then 2 mL of sample are dosed and titrated with the corresponding titrant while stirring. It is recommended to run each test in triplicates.

Table 2 and Table 3 show the parameters for the different determinations. The titrations for Ag and Pt electrodes are performed in DET mode, the titrations for Au electrodes in MET mode.

Table 2: Parameters for Ag and Pt electrodes

Mode	DET U
Measuring point density	4
Min. increment	10 μL
Dosing rate	Max
Signal drift	50 mV/min
Max. waiting time	26 s
Start volume	No
Pause	No
EP-recognition	All
Stop volume	3 mL
Stop U	Off
Stop EP	9
Filling rate	Max
Sample size	2 mL

Table 3: Parameters for Au electrodes

Mode	MET U
Signal drift	50 mV/min
Max. waiting time	10 sec
Volume increment	0.1 mL
Stop volume	3 mL
Stop U	Off
EP	9

Evaluation

The relative standard deviation of the determined values ($n=3$) should be less than 0.5 %.

Only one EP should be found per titration.

For each electrode type, criteria for passing the test are given in Table 4.

Table 4: Specification of electrodes

	Consumption (EP) [mL]	Potential jump [mV] $\Delta U_{90-110\%}$	Time [s]
Ag-electrodes	1.95 - 2.05	≥ 70	150
Pt-electrodes	1.95 - 2.05	≥ 70	150
Au-electrodes	1.95 - 2.05	≥ 70	160

The potential jump is calculated as follows:

$$FP\{1\} = EP \text{ volume} \times 0.9$$

$$FP\{2\} = EP \text{ volume} \times 1.1$$

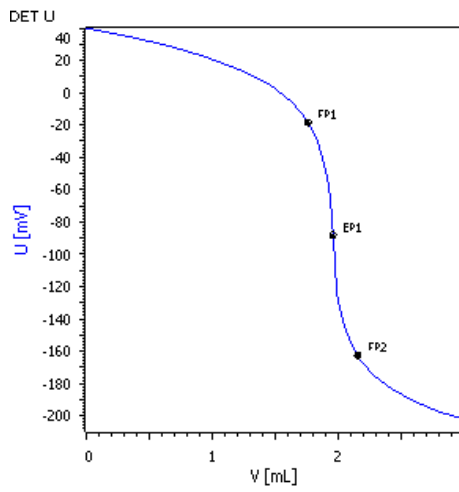
$$\Delta U_{90-110} = FP\{2\} - FP\{1\}$$

Remarks

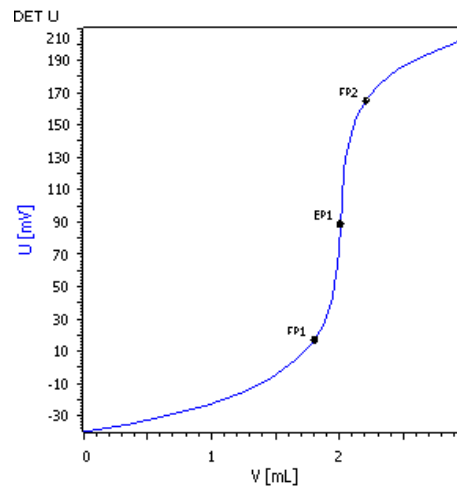
An electrode that measures an incorrect value is defective or contaminated in some way. Directions for cleaning of such electrodes are given in the corresponding instructions for use and monographs.

Curve examples

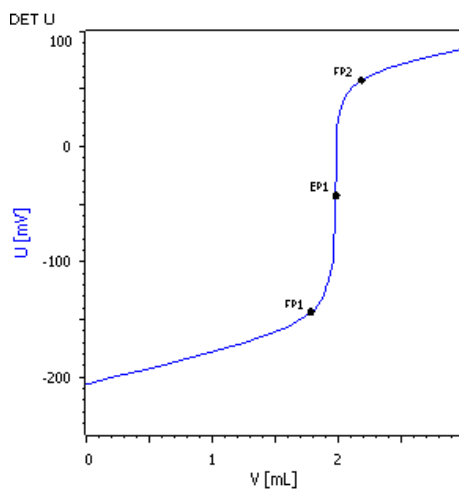
Ag Titrode



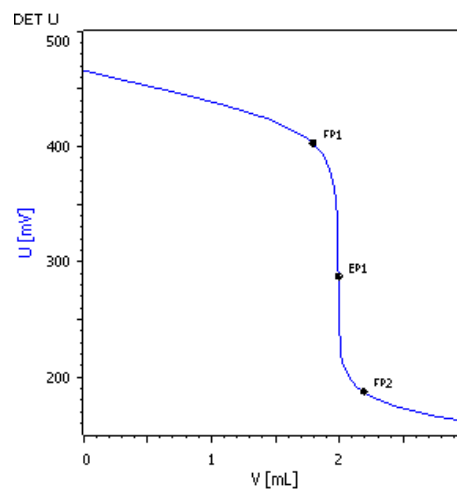
Ag-ring electrode



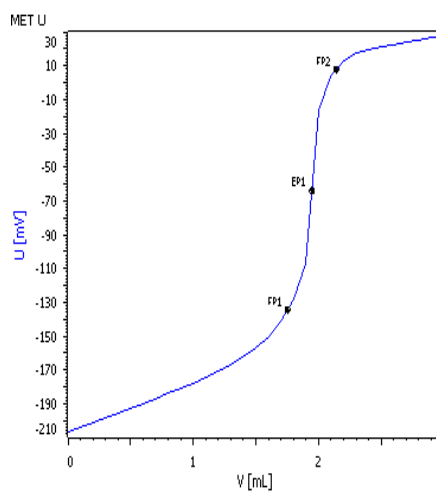
Pt Titrode



Pt-ring electrode



Micro Au Titrode



Au-ring electrode

